

TITLE: NOVEL SUPPORTED BIMETALLIC CARBIDE CATALYSTS FOR COPROCESSING COAL AND WASTE **DATE:** April, 1998

PIs: S. Ted Oyama, David F. Cox, Chunshan Song*

STUDENTS: Viviane Schwartz and Xinqin Wang, Ph.D. Candidates

INSTITUTIONS:	Virginia Tech	Penn State*
	Dept. of Chemical Engineering	Fuel Science Program
	Blacksburg, Virginia 24061-0211	University Park, PA 16802
	(540) 231-5309	(814) 863-4466

GRANT NO.: DE-FG26-97FT97265

PERIOD OF PERFORMANCE: October 1, 1997-April 15, 1998

OBJECTIVE: This project deals with the investigation of novel carbide catalysts for coal/waste coprocessing with a focus on understanding the fundamental chemistry related to the reaction pathways of coprocessing and the role of the catalysts in the conversion of coal/waste into liquid fuels. The catalysts to be tested are monometallic and bimetallic carbides of molybdenum, the most active of all the transition metal compounds in hydroprocessing. The initial stages of the project will involve preparation of catalysts and their screening with model reactions. In later stages the catalysts will be examined with real feeds, and the mechanism of reaction will be explored.

WORK DONE AND CONCLUSIONS:

Preparation and Testing of a Supported Bimetallic Nb-Mo Carbide

New studies on transition metal carbides and nitrides have demonstrated that the introduction of an additional metal or nonmetal elements into the binary phase can result in an improved performance over the original catalysts. Previous studies involved solely unsupported bimetallic carbides and nitrides. Since HDN and HDS reactions are structure sensitive, it was of interest to attempt to alter the catalytic surface by supporting the active phase on a support. Moreover, the catalytic properties of the carbide or nitride could be modified by the interaction with a support.

In the current investigation a new bimetallic oxycarbide supported system, Nb-Mo-O-C /Al₂O₃ (Mo/Nb = 1.6), was synthesized by the temperature programmed synthesis (TPS) technique. The supported bimetallic material was further characterized by CO chemisorption, BET surface area measurements, X-ray diffraction (XRD), near-edge X-ray absorption fine structure (NEXAFS) and reactivity in HDN and HDS reactions.

Mass spectrometer traces of H₂O (18) and CO (28) from the carburization process were used to show that the synthesis proceeded in several stages. The H₂O trace shows two low temperature peaks (402 and 650 K) related to the reduction of the oxide precursor. The CO signal also shows two small peaks in the low temperature region, as well as a single large peak at the isothermal

region. The latter is associated with carburization of the partially reduced oxide phase, with simultaneous further reduction followed by the carburization process.

The surface area of the synthesized Nb-Mo-O-C/ γ -Al₂O₃ (80 m²g⁻¹) was found to be close to that of the calcined γ -Al₂O₃ support. CO adsorption was used as a technique for titrating the number of uncoordinated surface metal atoms, and gave a value of 30 μ mol g⁻¹.

Since no peaks other than those associated with the support were identified in the diffraction pattern of the supported bimetallic material, little is known about the structure of the phase being formed on the support. TPR profiles of the supported bimetallic and the corresponding bulk bimetallic reference sample were similar indicating that the solid state reaction of these two materials were related. Therefore the XRD profile of the bulk reference sample probably gives a good representation of the material that is obtained after carburization of the supported oxide. Comparison of the XRD patterns indicate that the product of carburization is predominantly a bimetallic carbide, with small impurities of Mo₂C and a partially reduced niobium oxide (NbO₂).

The surface composition of the supported bimetallic Nb-Mo was characterized using NEXAFS in collaboration with Dr. J. Chen of the Exxon Corporate Labs. The C K-edge region of this catalyst is characterized by the typical carbidic resonances t_{2g} , e_g and ($a_{1g} + t_{1u}$) due to the transition of a C 1s electron to hybridized orbitals (C 2p_{x,y} + Nb/Mo 4d) and (C 2p_z + Nb/Mo 4d), respectively. The relative intensities of these three carbidic resonances are different from those of the unsupported Nb-Mo oxycarbides, indicating that the electronic properties of the oxycarbide are modified by the interaction with the Al₂O₃ support. The 20% NbMo_{1.6}-O-C/ γ -Al₂O₃ catalyst demonstrated high activities for quinoline HDN and dibenzothiophene HDS.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Carbides are unique because they have properties similar to those of the precious metals, but are *resistant* to sulfur. Preliminary results are promising, with Nb-Mo carbide showing higher activity in HDN than a commercial catalyst.

PLANS FOR THE COMING YEAR: In the following year, studies of coprocessing of Mo₂C and the bimetallic Nb-Mo carbide on coal and polymeric materials will be undertaken.

HIGHLIGHT ACCOMPLISHMENTS: A new supported Nb-Mo material was prepared which had excellent activity in the hydroprocessing of a model feed. The electronic properties of the materials were probed with NEXAFS spectroscopy.

ARTICLES AND PRESENTATIONS:

1. "New Catalysts for Hydroprocessing: Bimetallic Oxynitrides", *J. Catal.* **1998**, 173, 1.
2. "New Catalysts for Hydroprocessing: Reactivity Studies", *J. Catal.* **1998**, 173, 10.
3. "Supported Bimetallic Nb-Mo Carbide: Synthesis, Characterization, and Reactivity", *Preprints Petroleum Division*, **1998**, 43, 72..

Articles and Presentations Crediting Grant DE-FG26-97FT97265

Papers

1. Supported Bimetallic Nb-Mo Carbide: Synthesis, Characterization and Reactivity
V. Schwartz, S. T. Oyama, J. G. Chen
ACS Division of Petroleum Chemistry **1998**, 43, 72.
2. New Catalysts for Hydroprocessing: Bimetallic Oxynitrides $M_I-M_{II}-O-N$ ($M_I, M_{II} =$ Mo, W, V, Nb, Cr, Mn, and Co) Part I: Synthesis and Characterization.
C. C. Yu, S. Ramanathan and S. T. Oyama
J. Catal. **1998**, 173, 1.
3. New Catalysts for Hydroprocessing: Bimetallic Oxynitrides $M_I-M_{II}-O-N$ ($M_I, M_{II} =$ Mo, W, V, Nb, Cr, Mn, and Co) Part II: Reactivity Studies.
C. C. Yu, S. Ramanathan and S. T. Oyama
J. Catal. **1998**, 173, 10.

Presentations

1. "Synthesis and Reactivity of Niobium Molybdenum Oxycarbide, a New High-Activity Hydroprocessing Catalyst", 215th ACS National Meeting, Dallas Texas, Symposium on Advances in Heteroatom Removal, U. S. Ozkan, M. Daage, G. Antos, H. Topsoe, Organizers. March 29-April 2, 1998.
2. "Studies on Single Crystal Molybdenum Carbide", Tristate Catalysis Meeting, Charleston, West Virginia, April 20, 1998.